

EXHIBIT 45



Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid[☆]

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Abstract

The thermolysis of perfluorooctanoic acid ($\text{CF}_3(\text{CF}_2)_6\text{COOH}$) has been studied kinetically by high-temperature gas-phase NMR in both sodium borosilicate glass and quartz ampoules. In both cases, 1-H-perfluoroheptane is the major product, but the decomposition is considerably slower in quartz. The decomposition in borosilicate ampoules at 307 °C is greatly accelerated by the presence of crushed borosilicate glass and the reaction appears to be completely heterogeneous. Perfluoro-1-heptene is produced as a minor product and time-of-flight secondary ion mass spectrometry (ToF-SIMS) examination of the inner surface of the borosilicate glass ampoule after reaction reveals the presence of NaF. The thermolysis in quartz ampoules was studied by ex situ heating in the temperature range 355–385 °C and produced moderate amounts of perfluoro-1-heptene and SiF_4 in addition to 1-H-perfluoroheptane. Thermolysis in the presence of added crushed quartz accelerates the decomposition, as does increasing the concentration of perfluorooctanoic acid or carrying out the thermolysis in the presence of water. The thermolysis of perfluorooctanoic acid thus proceeds at widely different rates depending on concentration and on the physical and chemical environment. By contrast, the pyrolysis of ammonium perfluorooctanoate is more facile by orders of magnitude and proceeds by first-order kinetics at essentially the same rates in both quartz and borosilicate ampoules with an estimated half-life of 2 s at 307 °C.

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1. Introduction

Ammonium perfluorooctanoate (APFO) is a surfactant commonly used as a processing aid in the production of fluoropolymers and fluoroelastomers [1–3]. As a class of surfactants, perfluorocarboxylates (PFCAs) and perfluorosulfonates are remarkably stable and it is this property, that makes them useful in many applications [1]. It has been asserted that PFCAs have no known environmental degradation pathway [4]. It has recently been shown that APFO does not survive the elevated temperatures (350–400 °C) specified for fluoropolymer processing [5]. We were, therefore, interested to examine the thermal stability of the related PFCA, perfluorooctanoic acid.

The mechanism for thermolysis of trifluoroacetic acid (TFA, the lowest PFCA homolog) in the gas phase has been examined previously and these studies [6–9] have shown that the decomposition reaction is both complex and subject to wall effects (surface assistance). By analogy with the rates of decarboxylation of TFA and its anion under hydrothermal conditions [10], it seems likely that undissociated perfluorooctanoic acid is thermally more stable than any of its salts. Due to the low $\text{p}K_a$ of 1.5 for perfluorooctanoic acid [11], the anion is the dominant form expected to be present in solution. Conditions that suffice for the thermal decomposition of the free acid are, therefore, expected to exceed the conditions required for the thermolysis of any of its salts.

We have examined the kinetics of thermal decomposition of perfluorooctanoic acid using high-temperature gas-phase NMR. Gas-phase NMR has previously been used to study the chemical kinetics of a variety of processes [5,12–14]. While the acronym PFOA has been used in the literature either to represent the perfluorooctanoate anion or to refer ambiguously to either the acid or the salt, in this report the abbreviation

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PFOA for perfluorooctanoic acid ($\text{CF}_3(\text{CF}_2)_6\text{COOH}$) strictly refers to the free acid.

2. Results and discussion

Previous gas-phase NMR studies in our laboratory utilized sodium borosilicate glass ampoules (e.g., Ref. [5]). In view of the role of surface processes in the thermolysis of TFA [6–9], alternative materials were considered for the present study. Quartz ampoules flame-dried under vacuum provide the most inert reactor surface compatible with our gas-phase NMR method. A typical sample in a sealed quartz ampoule consisted of 32 mg of PFOA (77 μmol , m.p. $\approx 55^\circ\text{C}$, b.p. $\approx 200^\circ\text{C}$) and 23 μmol of C_2F_6 as internal mass and chemical shift standard. Assuming ideal gas behavior and an internal volume of 4.0 mL, the internal pressure at 307°C is close to 1 atm and the molar concentration of PFOA is approximately 0.02 M. The gas-phase ^{19}F NMR spectrum at 307°C shows six resolved CF_2 fluorine resonances and a resonance for the CF_3 fluorines.

In situ NMR kinetics at 307°C for 65 h in this relatively inert reactor led to approximately 4% conversion of PFOA, formation of approximately 2% of 1-H-perfluoroheptane [5] and a trace of SiF_4 . Proton NMR detection at the end of the reaction likewise revealed the formation of 1-H-perfluoroheptane (δ 5.76, ^1H , t, $J = 52$ Hz) as well as the formation of water (δ 0.60 in the gas phase). The concomitant formation of CO_2 (and possibly CO), containing neither proton nor fluorine, falls outside our methodology and is assumed; similarly, non-gas-phase reaction products are not observed.

PFOA decomposition at higher temperatures was investigated by ex situ heating in quartz ampoules since the temperatures for convenient kinetics exceed the in situ capabilities of our NMR probe. Heating of the ampoules was carried out in a furnace at 355, 370 and 385°C for appropriately chosen times, followed by quenching to room temperature. The extent of reaction was then monitored by ^{19}F NMR at 243°C . Thermal decomposition of PFOA at 355– 385°C gives two organofluorine products, 1-H-perfluoroheptane as the major one and perfluoro-1-heptene [15] as a minor one. SiF_4 also grows in as a product as the decomposition reaction proceeds.

The time evolution of the major reaction components in these ex situ experiments was fitted by first-order exponentials as shown in Fig. 1 for the kinetic run at 370°C . The integrated NMR intensity of the mass standard is invariant and is used to normalize the NMR intensities of the reaction components. The sum of the concentrations of the principal organic components (PFOA, 1-H-perfluoroheptane and perfluoro-1-heptene) decreases slightly during the kinetic run (vide infra). Similar first-order fits were obtained for the kinetics at 355 and 385°C .

The pseudo first-order rate constants for loss of PFOA, formation of 1-H-perfluoroheptane and formation of perfluoro-1-heptene are presented in Table 1. The estimated half-life for PFOA at 385°C is 26 min under these conditions. Evidence for lack of truly first-order behavior was obtained by an analogous kinetic run at 370°C in which the amount of starting PFOA was

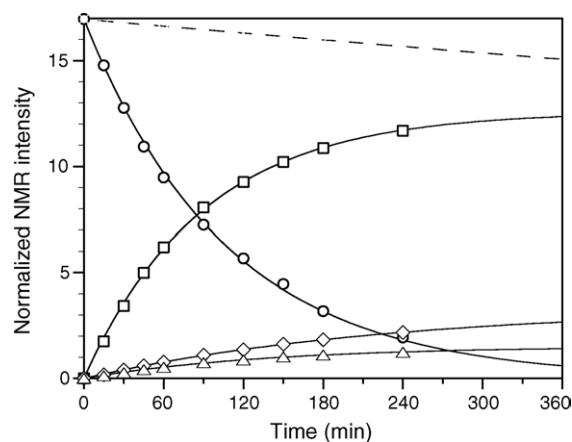


Fig. 1. Kinetics of gas-phase PFOA (\circ) decomposition at 370°C in a quartz ampoule and appearance of 1-H-perfluoroheptane (\square), perfluoro-1-heptene (\diamond) and SiF_4 (\triangle). The linear best fit of the mass balance (dashed line) represents the sum of the NMR intensities of PFOA, 1-H-perfluoroheptane and perfluoro-1-heptene.

tripled. Essentially, all PFOA (96 mg) was decomposed in about 2 h instead of about 9 h (32 mg), indicating that molecular associations play an accelerating role at higher concentrations. Similarly, decomposition was markedly accelerated at 365°C by the presence of two equivalents of added water and was complete in about 45 min.

Decomposition of carboxylic acids in the gas phase is prone to heterogeneous effects and surface assistance [16]. In order to evaluate the role of quartz in the observed kinetics, the in situ thermolysis of PFOA at 307°C was repeated in the presence of approximately 320 mg of flame-dried crushed ampoule quartz as a means of increasing the surface-to-volume ratio. The reaction was substantially accelerated by the presence of the crushed quartz (Fig. 2), demonstrating that heterogeneous reactions are likely also to play a role in the quartz ampoules used for the ex situ kinetic runs. Approximately, 30% conversion of PFOA was obtained after 65 h, in contrast to only 4% conversion observed in the absence of crushed quartz. 1-H-Perfluoroheptane and SiF_4 are the most visible products, growing steadily as the reaction proceeds and there are only traces of perfluoro-1-heptene ($<1\%$) at the end of the kinetic run.

The top line in Fig. 2 represents the time dependence of the normalized intensity of the CF_3 fluorine resonance (-81.2 ppm) that incorporates the CF_3 signals of all species in the vapor phase having CF_3 -terminated perfluoroalkyl chains, as these CF_3 fluorines all have the same chemical

Table 1

Apparent first-order rate constants for gas-phase decomposition of PFOA in quartz ampoules

Temperature ($^\circ\text{C}$)	$k \times 10^3$ (min^{-1})		
	PFOA	$\text{CF}_3(\text{CF}_2)_5\text{CF}_2\text{H}$	$\text{CF}_3(\text{CF}_2)_4\text{CF}=\text{CF}_2$
355	5.0 ± 0.7^a	7.0 ± 1.8	1.8 ± 0.9
370	9.2 ± 0.7	11.1 ± 1.2	4.3 ± 0.9
385	26.4 ± 3.1	23.0 ± 2.1	8.9 ± 4.5

^a Errors represent one standard deviation.

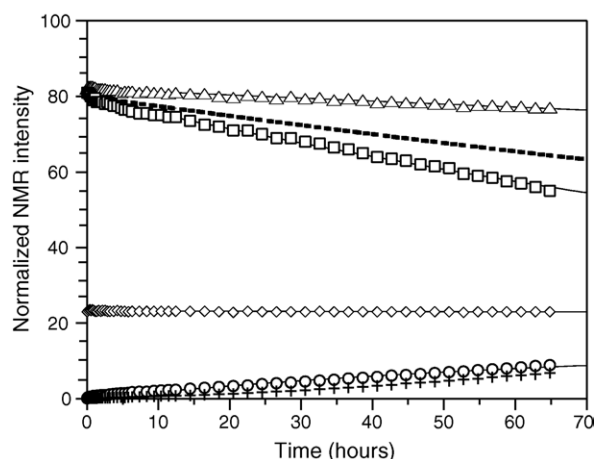
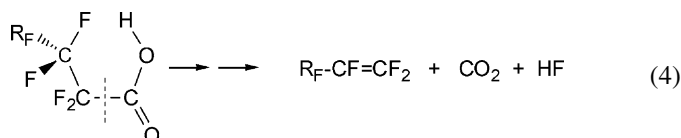
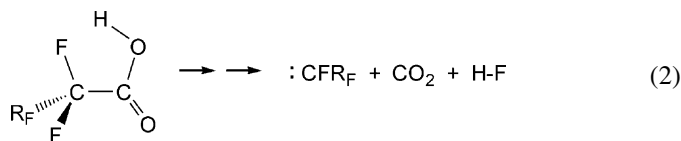
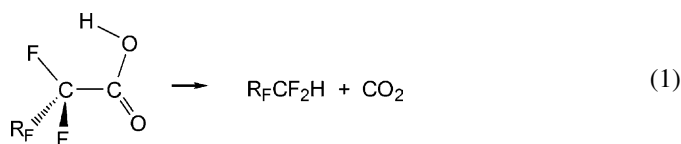


Fig. 2. Kinetics of gas-phase PFOA (\square) decomposition at 307 °C in a quartz ampoule containing approximately 320 mg of crushed quartz. The appearance of 1-H-perfluoroheptane (\circ), SiF_4 (+) and the constant intensity of the C_2F_6 standard (\diamond) are indicated. The dashed line is the sum of the NMR-derived concentrations of PFOA and 1-H-perfluoroheptane. The upper line (\triangle) is the normalized NMR intensity of the terminal $-\text{CF}_3$ fluorine resonance common to all long-chain species in the vapor phase.

shift. By the end of the 65 h reaction time, the intensity of this signal drops by about 7%, indicating a loss of such CF_3 -containing molecules from the gas phase. The NMR intensities of PFOA and 1-H-perfluoroheptane, on the other hand, add up to the dashed line in Fig. 2. There are thus unaccounted molecules with overlapping CF_3 resonances in the vapor phase. Indeed, several minor peaks grow steadily during the course of the kinetics, but have not been positively assigned: δ ppm (relative strength) -67.0 (vw), -70.4 (w), -137.3 (vw), -153.5 (vw), -157.2 (vw), -163.1 (w), -163.8 (w). In the spectral region of $-\text{CF}_2$ resonances there are additional growing peaks obscured by severe overlap. The chemical shifts -67.0 and -70.4 are very close to the chemical shifts for *cis* and *trans* perfluoro-2-butene [12] and the remaining chemical shifts are appropriate for *cis* and *trans* vinylic fluorines [17]. Isomerized internal perfluoroheptenes, particularly 2-perfluoroheptene, are, therefore, candidates for the unaccounted species.

It is appropriate to consider the possible initiating unimolecular processes (Eqs. (1) and (2)) analogous to those considered in the pyrolysis of TFA ($R_F = \text{F}$) [6–9,18]. Decomposition via a four-membered transition state (Eq. (1)) was excluded both experimentally and theoretically and may likewise be excluded for PFOA ($R_F = \text{CF}_3(\text{CF}_2)_4\text{CF}_2$). Elimination of HF via a five-membered transition state (Eq. (2)) with the formation of difluorocarbene ($R_F = \text{F}$) was accepted as the initial step for TFA decomposition and formation of CF_3H , analogous to 1-H-perfluoroheptane, was ascribed to the insertion of difluorocarbene into the H–F bond (Eq. (3), $R_F = \text{F}$). In the case of PFOA, Eq. (2) would lead to fluoro(perfluorohexyl) carbene ($:\text{CF}(\text{CF}_2(\text{CF}_2)_4\text{CF}_3)$). In contrast to TFA, longer-chain perfluorocarboxylic acids have the potential to decarboxylate with loss of HF via a six-membered transition state to produce the corresponding terminal perfluoroalkene (Eq. (4)).



The results obtained with added crushed quartz unmistakably implicate heterogeneous accelerating processes on quartz and make it impossible to distinguish between heterogeneous and homogeneous reactions in the thermal decomposition of PFOA under the current conditions. Accordingly, the temperature dependence of the gas-phase NMR kinetics presented in Table 1 cannot be interpreted mechanistically. The apparent activation parameters obtained from this kinetic data for PFOA decomposition are $E_a = 197 \text{ kJ mol}^{-1}$ and $\log(A/\text{s}^{-1}) = 12.2$. The rate of gas-phase decomposition of PFOA is, therefore, expected to vary depending upon the nature of the surface available.

A surface reaction occurring in unison with the formation of 1-H-perfluoroheptane and 1-perfluoroheptene is the formation of SiF_4 on the quartz (silica) surface (Fig. 1) and is anticipated to involve HF. The formation of commensurate amounts of water ($\text{SiO}_2 + 4\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{SiF}_4$) and the probable isomerization of perfluoroheptene are both consistent with the involvement of HF, as required by Eqs. (2) and (4) or by their heterogeneous analogs.

Since the fluorine mass balance in the vapor phase slowly decreases with time (Fig. 2), the presence of involatile fluorine-containing species was sought by time-of-flight secondary ion mass spectrometry (ToF-SIMS) mapping of the inner wall of the reacted quartz ampoule. In contrast to an unreacted ampoule, which appeared relatively uniform, the reacted ampoule was decorated with domains of high ion-yield that were approximately 30 μm in diameter. Mass spectra extracted from these domains revealed several progressions of mass peaks from approximately 1000–1500 Da differing in mass by 50 Da appropriate for CF_2 fragments. The formation of high-molecular weight species is consistent with the involve-

ment of carbenoid intermediates that can lead to polymers [19,20].

The above evidence for heterogeneous reactions on silica suggested that PFOA decomposition could behave differently in ampoules made of sodium borosilicate glass. The kinetics of thermolysis of PFOA in such an ampoule at 307 °C is presented in Fig. 3. The concentration of olefin is approximately 5% that of 1-H-perfluoroheptane and the mass balance indicates that formation of 1-H-perfluoroheptane and perfluoro-1-heptene completely accounts for the loss of PFOA. Considering that in a quartz ampoule, only 4% conversion of PFOA was observed after 65 h at the same temperature, it is clear from Fig. 3 that sodium borosilicate glass strongly accelerates the decomposition of PFOA relative to quartz. In contrast to the analogous decomposition in quartz (Fig. 1), SiF₄ was either absent or present in trace amounts, in similar experiments in borosilicate glass.

The time dependence in Fig. 3 is unusual in that it appears to be bimodal and suggests that surface sites that are initially capable of catalyzing the decomposition reaction are being deactivated. A simple model starting with a first-order equation in which the rate constant is allowed to be time-dependent and to decrease in time in proportion with the number of converted molecules leads to decays that can be represented by a sum of two first-order exponentials.

In the limit of a much larger number of active sites relative to reactant molecules, pseudo first-order is obtained. In the opposite limit, when there are more reactant molecules than active sites, the rate tends to zero when all sites are deactivated and the reaction greatly slows down. The data presented in Fig. 3 can be fitted reasonably well by this model, but the fitting parameters have no general significance since they refer only to this specific set of experimental conditions.

Further evidence for the involvement of surface sites in the decomposition of PFOA in borosilicate glass was obtained by carrying out the kinetics in the presence of crushed borosilicate glass in order to increase the surface-to-volume ratio. When the

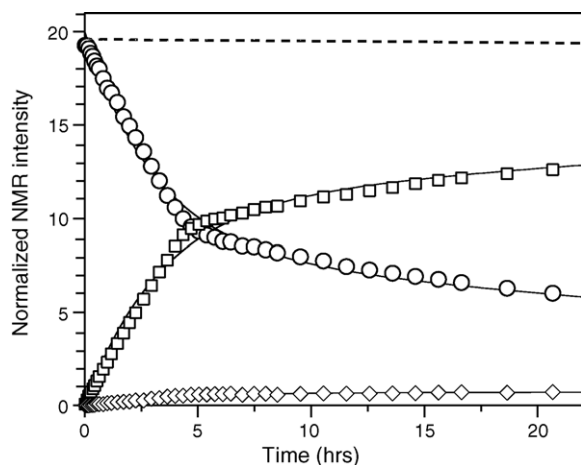


Fig. 3. Kinetics of gas-phase PFOA (○) decomposition at 307 °C in a sodium borosilicate glass ampoule and formation of 1-H-perfluoroheptane (□) and perfluoro-1-heptene (◇). The mass balance (dashed line) was estimated from the sum of the NMR-derived organofluorine concentrations.

thermolysis experiment at 307 °C was repeated in the presence of approximately 370 mg of this crushed glass, the decomposition was faster than any observed so far under our conditions at this temperature. Approximately, 90% of the PFOA was consumed in the first 4.5 h and after a total of 8 h, 99% of the PFOA was consumed (Fig. 4) compared with only 30% conversion after 65 h at the same temperature under analogous conditions in quartz. 1-H-Perfluoroheptane and perfluoro-1-heptene were formed as the major products during the first 4.5 h and no significant further reactions took place (attesting the stability of the products under these conditions). Only traces of SiF₄ were observed and the relative yield of the olefin was substantially greater than in the absence of crushed glass. Proton NMR examination after the reaction revealed the characteristic –CF₂H proton resonance of 1-H-perfluoroheptane and a peak for water at 0.6 ppm. Comparison of the fluorine and proton spectra indicated that water was formed in an amount equivalent to the olefin.

The thermolysis of PFOA in the presence of crushed glass corresponds to the regime where active surface sites are in large excess relative to reactant molecules. Under these conditions, the decay of PFOA and the formation of both 1-H-perfluoroheptane and perfluoro-1-heptene, follow pseudo first-order kinetics with very similar rate constants of 9.0×10^{-3} , 9.8×10^{-3} and $7.9 \times 10^{-3} \text{ min}^{-1}$, respectively (in agreement with the theory for parallel first-order reactions [21]).

The decompositions of PFOA in quartz and in borosilicate glass differ in another respect. While SiF₄ is a product of reaction growing in unison with the two major organofluorine products in quartz, it is essentially absent in borosilicate glass. To produce the olefin, it is necessary to lose a fluorine for which there is no evidence in the gas phase given the mass balance (Fig. 4). It may be considered that the fluorines removed to make perfluoro-1-heptene react with and stay on the borosilicate glass. One key difference between silica and borosilicate glass is the presence of sodium ions in the latter. It is, therefore, probable that the sodium salt of PFOA is formed by reaction of the acid with the surface (forming water) and

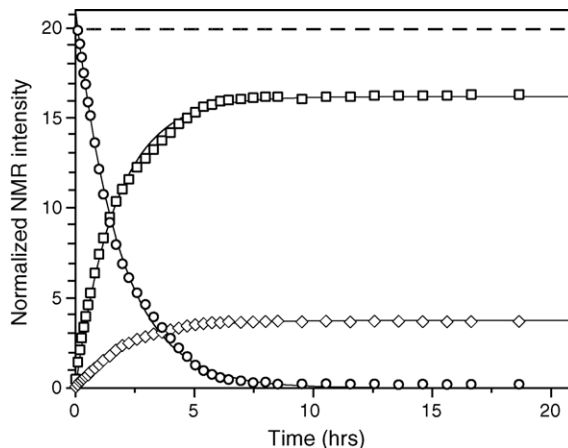
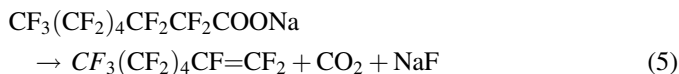


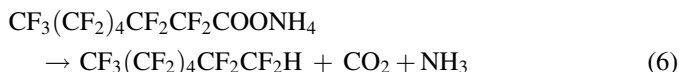
Fig. 4. Kinetics of gas-phase PFOA (○) decomposition at 307 °C in a sodium borosilicate glass ampoule in the presence of crushed glass and formation of 1-H-perfluoroheptane (□) and perfluoro-1-heptene (◇).

then easily decomposes pyrolytically to the olefin (Eq. (5)) as is well known for such salts [22,23]:



ToF-SIMS mapping of a segment of the inner surface of the borosilicate ampoule supports the notion of this surface reaction. This technique revealed more or less continuous fluorine-containing domains, which were absent in an unreacted ampoule. The mass spectral data associated with these areas showed evidence for formation of sodium fluoride arising from the fluorine removed to form the fluoroolefin. In total, these results indicate that the thermal decomposition of PFOA in the presence of sufficient borosilicate glass is a heterogeneous process.

Previously, the in situ thermolysis of solid ammonium perfluorooctanoate was studied by monitoring the evolution of 1-H-perfluoroheptane (Eq. (6)) in sodium borosilicate glass ampoules using gas-phase ^{19}F NMR [5]. This study estimated $E_a = 154 \pm 11 \text{ kJ mol}^{-1}$ and $\log(A/s^{-1}) = 13.6 \pm 1.2$ (error estimates represent 95% confidence limits). It was, therefore, of interest to examine APFO thermolysis in flame-dried quartz ampoules in order to ascertain whether the APFO decomposition process was also sensitive to the type of reactor surface.



The decomposition of APFO in quartz was studied in the same temperature range as employed previously (196–234 °C) using the same amounts of starting material and 79 μmol C_2F_6 internal mass standard. Although the observed rate constants in quartz were slightly smaller than found previously, the associated activation parameters ($E_a = 150 \text{ kJ mol}^{-1}$ and $\log(A/s^{-1}) = 13.0$) are well within the error limits estimated previously [5]. Modest amount of perfluorooctanamide, $\text{CF}_3(\text{CF}_2)_6\text{CONH}_2$, were also observed. The yield of this minor product was found to decrease monotonically as the temperature was increased and extrapolation indicates that the yield of this minor product would be near zero at 270 °C.

The above observations indicate that the kinetics of decomposition of APFO is relatively well-behaved, in contrast to the results observed for PFOA. The activation parameters for the decomposition of APFO in quartz ampoules may be used to estimate a half-life of 2 s at 307 °C.

3. Conclusions

PFOA in an isolated environment is thermally quite stable up to 300 °C, but at higher temperatures is susceptible to decomposition at increased rates via heterogeneous assistance. The half-life of PFOA at 307 °C in the presence of crushed quartz under our conditions may be estimated as 5 days, whereas in the presence of crushed sodium borosilicate glass,

the half-life at this temperature is approximately 1.3 h. Increasing the concentration of PFOA, as well as carrying out the decomposition in the presence of water, accelerates the reaction, indicating that molecular associations provide more facile decomposition pathways. The thermal decomposition of perfluorooctanoic acid thus proceeds at widely different rates depending on concentration and on the physical and chemical environment. By contrast, the pyrolysis of the ammonium salt, APFO, is more facile by orders of magnitude and proceeds by first-order kinetics at essentially the same rates in both quartz and borosilicate ampoules. From the derived activation parameters, a half-life of 2 s at 307 °C is estimated for APFO. It is anticipated that most other salts of PFOA will thermally decompose at temperatures substantially lower than those required for the free acid [22,23].

4. Experimental

Since details of the gas-phase NMR apparatus and methodology have been described previously [5,13,24], only a brief outline is presented here. Gas-phase NMR ampoules were made from 6.5 cm sections of 10 mm o.d. NMR tubes (borosilicate glass or quartz) fitted with a 5 mm o.d. extension which served to attach the ampoule to a vacuum system for sample loading or to center the sealed ampoule in the thermostated region of the NMR probe (Fig. 5). Micromolar quantities of PFOA were weighed into the ampoule and a reference gas (C_2F_6) was transferred in known micromolar

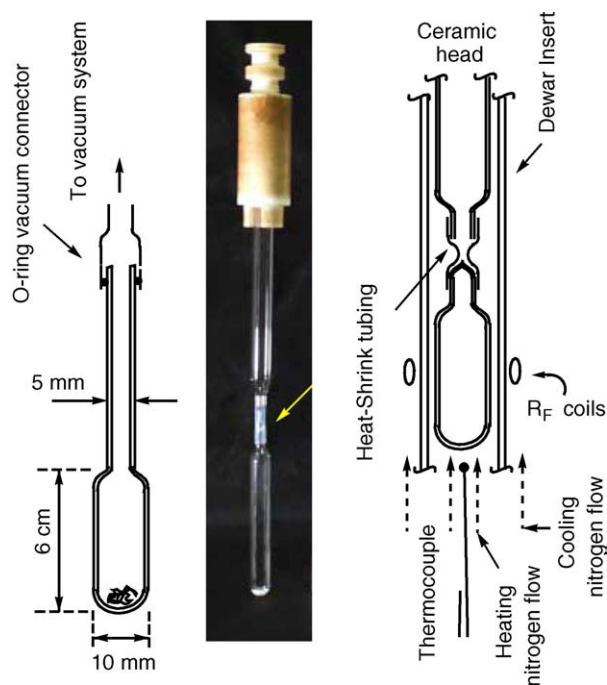


Fig. 5. Diagram of the gas-phase NMR ampoule attached to a vacuum system before being sealed off with a propane torch (left). Center: the sealed ampoule attached by means of heat-shrink tubing to a matching 5 mm o.d. glass stub of the holding-tube, which rests within a ceramic head. The ampoule assembly is lowered into the magnet using a string. The amount of sample material is chosen so that the internal pressure after complete vaporization will not exceed a safe limit (<1.5 atm).

amounts prior to sealing the ampoule with a torch; the internal volume after sealing was approximately 4.0 mL. The added gas served not only as a chemical shift reference but also as a mass reference. The starting number of micromoles of PFOA was obtained from the weight and was compared with the micromoles of the C_2F_6 mass standard (as obtained from the ^{19}F NMR intensity) in order to define the starting point for the kinetics. The integrated NMR intensity of the mass standard was invariant and was used to normalize the NMR intensities of the reaction components. Ampoules were obtained from New Era Enterprises Inc. (Vineland, NJ) and were either kept in a vacuum oven at 110–120 °C or were flame-dried on a vacuum line ($P < 1$ mTorr) before use.

The ^{19}F NMR spectra were obtained using a 400 MHz Oxford magnet (^{19}F at 376.312 MHz) with a Varian Unity Inova console. The high-temperature 10 mm probe and variable temperature controller had a nominal upper temperature rating of 400 °C and were purchased from Nalorac Corporation (now Varian Inc.). It was found that in situ kinetic studies lasting more than a few hours were limited to sample temperatures of 307 °C or less in order to avoid exceeding the upper temperature limit of the shim stack (110 °C). ^{19}F NMR spectra were acquired using a small flip-angle pulse ($\sim 35^\circ$) in order to achieve relatively uniform power distribution over the appropriate spectral region. ^{19}F chemical shifts in the gas phase were measured relative to C_2F_6 at -87.2 ppm on the $CFCl_3$ (F11) scale. Since ^{19}F spin-rotation relaxation is very efficient in the gas phase, 250 ms recycle delays were appropriate and permitted rapid signal averaging (e.g., 180 scans in approximately 1 min). Temperatures were calibrated using a thin thermocouple positioned in the center of a dummy ampoule identical to those used for the actual kinetic runs except for a small hole at the end of the 5 mm stem to permit insertion of the thermocouple.

The gas-phase ^{19}F NMR spectrum of PFOA at 243 °C consisted of six CF_2 fluorine resonances in the region from -116.4 to -123.9 ppm and a resonance for the CF_3 fluorines (-81.2 ppm). 1-H-Perfluoroheptane [5] and perfluoro-1-heptene [15] were recognized by resonances that were distinct from those of PFOA (e.g., terminal $-CF_2H$ and perfluorovinyl fluorines, respectively). Perfluorooctanamide ($CF_3(CF_2)_6CONH_2$) was identified by its 1H and ^{19}F NMR spectra which were identical to those of a commercial sample obtained under conditions similar to those used for the kinetic studies. The CF_3 resonances of the latter three compounds overlapped that of PFOA. SiF_4 was observed at -169.2 ppm.

Kinetic studies which were performed at temperatures exceeding 307 °C were conducted by placing the ampoule for specified time intervals in a furnace consisting of a cylindrical copper body with a 12 mm bore and holes for thermocouple placements surrounded by heater wire coils embedded in ceramic insulation. The temperature controller was from Electronic Control Systems Inc. (Poway, CA). Furnace temperatures were checked with a digital thermometer and agreed within 1 °C up to 400 °C with the temperature read by the controller. Because of the small heat capacity of the ampoules, thermal equilibrium was reached in a time much

shorter than the heating intervals. After a fixed period of time in the furnace, the ampoule was removed and quickly cooled to room temperature by covering the ampoule with sand to quench the pyrolysis. The ampoule was then placed in the NMR probe at 243 °C, a temperature above the boiling point of PFOA but at which decomposition was very slow, and the ^{19}F NMR spectrum acquired as described above.

Time-of-flight secondary ion mass spectrometry data were acquired with an Ion-ToF GmbH Model IV ion-reflector type time-of-flight instrument (Muenster, Germany). Au^+ primary ions were used and a pulsed electron flood gun was used for charge compensation. Spatially-resolved ToF-SIMS spectral data was acquired in 256 pixel \times 256 pixel arrays spanning 500 $\mu m \times$ 500 μm areas from the inside surfaces of ampoules. Positively- and negatively-charged secondary ions were collected in separate experiments. Analysis was carried out on the inner surface of both reacted and unreacted ampoules.

Linear PFOA (97% purity) was obtained from Oakwood Products Inc. and was dried in a desiccator and kept in a nitrogen glove box. 1-H-Perfluoroheptane (1-H-pentadecafluoroheptane) was purchased from Lancaster Synthesis Inc. and hexafluoroethane (F116) was prepared in our laboratories. Tetramethylsilane (TMS) and perfluorooctanamide were purchased from Aldrich and used without further purification. Perfluoro-1-heptene ($>95\%$ purity) was purchased from SynQuest Laboratories Inc.

Acknowledgments

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